Minimum-Time Strategy to Produce Nonuniform Emulsion Copolymers. I. Theory

JOSE C. DE LA CAL, ANTONIO ECHEVARRIA, GREGORIO R. MEIRA, and JOSE M. ASUA*

Grupo de Ingeniería Química, Departamento de Química Aplicada, Facultad de Ciencias Químicas, Universidad del País Vasco, Apdo. 1072, 20080 San Sebastián, Spain

SYNOPSIS

A method for calculating the optimal monomer addition policy to produce emulsion copolymers with a given composition profile is presented. The approach allows the calculation of the time evolution of the monomer feed rates that ensure the formation of the desired copolymer composition profile in a minimum process time. The method was applied by simulation to obtain widely different copolymer composition profiles during the emulsion copolymerization of butyl acrylate and styrene. The results were compared with those obtained by means of the power feed method. In these calculations, it was assumed that both the kinetic model and the values of the kinetic parameters are available. The implementation of this approach to real emulsion copolymerization systems in which only a limited kinetic information is available is presented in the second article of this series. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Specialty products such as paints, adhesives, and binders require strict specifications of the corresponding latexes. In particular, the composition of the emulsion copolymers exerts a powerful effect on the properties of the particles and resultant films. Consequently, one way to obtain specific products is the control of the composition of the copolymers. In some applications, a homogeneous copolymer is needed, whereas in others, a gradient of copolymer composition is more useful.

Traditionally, the control of the composition of the copolymers has been achieved through semicontinuous emulsion polymerization carried out under starved conditions.[1-5] In this process, a stream with a mixture of monomers of the same composition as that desired for the copolymer is fed into the reactor at a very low flow rate. In this way, the rate of polymerization is practically equal to the monomer feed rate and this results in a copolymer of the same composition as that of the feed. An additional ad-

vantage of the starved process is that the heat-generation rate is easily controlled. Following this process, if a nonuniform copolymer is desired, a continuous change of the composition of the monomer mixture feed is required. Several arrangements for gradually changing the monomer mixture composition of the feed stream entering the reactor have been reported.[3] This method, the so-called power feed method, is based on the use of two or more monomer storage tanks before the reaction vessel, each one working at a constant feed rate. The tanks are disposed in series in such a way that the composition of the mixture of monomers changes continuously in all tanks between the reactor and the first tank. The nature of the variation in composition is controlled by suitable choices of simple variables such as the initial monomer weight and initial monomer composition in the tanks. In this way, a two-tank arrangement permits composition profiles which vary smoothly in one direction, whereas a three-tank arrangement leads to inflections and composition reversals. Variable feed rates of both monomers can also be employed to generate similar profiles.

Although low monomer concentrations in the polymer particles can give relatively high polymer-

---

ization rates due to the gel effect, under starved conditions, the concentration of the monomers in the polymer particles is very low and, consequently, the slow polymerization rates can lead to long process times. To overcome this problem, a different monomer addition strategy for producing homogeneous copolymers has been proposed.[6,7] In this so-called semistarved process, the reactor was initially charged with all of the less reactive monomer plus the amount of the more reactive monomer needed to initially form a copolymer of the desired composition. Then, the remaining more reactive monomer was added at a time-dependent flow rate that ensured the formation of a homogeneous copolymer. Using this strategy, a homogeneous copolymer was formed in a minimum process time. However, no minimum-time approach for obtaining emulsion copolymers of nonuniform composition has been reported.

This problem is addressed in this series of articles. In the first, a method for calculating the optimal monomer addition policy to produce a well-defined copolymer composition profile is presented. The optimal monomer addition policies to obtain widely different copolymer composition profiles during the emulsion polymerization of butyl acrylate and styrene were calculated by simulation and the results compared with those obtained by means of the power feed method. In the second, the optimal monomer addition policies were implemented experimentally in an open-loop control scheme for the emulsion copolymerization of butyl acrylate and styrene.

OPTIMIZATION APPROACH

Let us assume that a latex with a given solids content, S_c (g/cm^3 of water), and instantaneous copolymer composition profile, $Y_A(X_T)$, was desired. The average copolymer composition at the end of the process is given by

$$\bar{Y}_{A_T} = \int_0^1 Y_A(X_T)\, dX_T \tag{1}$$

where X_T is the overall conversion, defined as the ratio of the monomer incorporated to the copolymer at any time and the total monomer.

The total amount of each monomer per unit volume of water is easily determined by the following equations:

$$S_c = B_T M_{W_B} + A_T M_{W_A} \tag{2}$$

$$B_T = \frac{A_T(1 - \bar{Y}_{A_T})}{\bar{Y}_{A_T}} \tag{3}$$

where A_T and B_T are the total amounts (mol/cm^3 of water) of monomers A and B, respectively, and M_{W_i} the molecular weight of monomer i.

In addition, a copolymerization system with the following characteristics is assumed:

(i) Seeded copolymerization of monodisperse spherical particles with average composition $\bar{Y}_A(0)$.
(ii) Constant number of polymer particles during the processes.
(iii) Negligible aqueous phase polymerization.
(iv) Monomers distributed between phases according to thermodynamic equilibrium.

The goal is to determine the addition rate of monomers A and B that ensures a copolymer composition profile $Y_A(X_T)$ in a minimum end-time. This optimization problem reduces to the minimization of the following objective function:

$$F = \int_0^1 \frac{1}{R_p}\, dX_T \tag{4}$$

where R_p is the overall polymerization reaction rate, and X_T, the overall conversion.

In addition, the optimization must be subjected to the following equality and inequality constraints at any conversion value:

(i) *The copolymer produced must have the desired composition:*

$$\frac{Y_A(X_T)}{1 - Y_A(X_T)} = Y(X_T) = \frac{R_{p_A}(X_T)}{R_{p_B}(X_T)} \tag{5}$$

where R_{p_i} is the polymerization rate of monomer i per unit volume of water given by

$$R_{p_i} = -(k_{p_{A_i}} P_A^P + k_{p_{B_i}} P_B^P)[i]_p \frac{\bar{n} N_p}{N_A} \tag{6}$$

where $k_{p_{ij}}$ are the propagation rate constants; $[i]_p$, the concentration of the monomer i in the polymer particles; n, the average number of radicals per particle; N, the number of particles per cm^3 of water; N_A, the Avogadro's number; and P_i^P, the time-average probabilities of finding a free radical with ul-

timate unit of type i in the polymer particles. These probabilities are given by[8]

$$P_A^P = \frac{k_{pBA}[A]_p}{k_{pBA}[A]_p + k_{pAB}[B]_p} \qquad (7)$$

$$P_B^P = 1 - P_A^P \qquad (8)$$

The ratio $[A]_p/[B]_p$ that ensures a copolymer composition profile $Y_A(X_T)$ can be obtained combining eqs. (5)–(8) as follows:

$$\left(\frac{[A]_p}{[B]_p}\right)(X_T)$$

$$= \frac{[Y(X_T) - 1] + \{[Y(X_T) - 1]^2 + 4r_A r_B Y(X_T)\}^{0.5}}{2r_A}$$

$$= \beta(X_T) \quad (9)$$

where r_A and r_B are the reactivity ratios of monomers A and B, respectively. For each overall conversion X_T, eq. (9) gives the ratio of the concentrations of the monomers in the latex particles.

(ii) *The concentrations of monomers into the latex particles should be equal or less than the concentration of saturation, namely, the presence of monomer droplets was not allowed.*

The excess of monomer which is in the monomer droplets does not contribute to increase the polymerization rate but causes a significant loss of control capacity. The maximum concentrations of the monomers in the latex particles are those corresponding to the saturation and can be calculated from the monomer equilibrium equations and the overall material balances when the first droplet is formed.

When partition coefficients are used, the equilibrium equations are as follows:

$$k_{j,k}^i = \frac{\phi_i^j}{\phi_i^k} \qquad (10)$$

where $k_{j,k}^i$ is the partition coefficient of monomer i between phases j and k, and ϕ_i^j and ϕ_i^k, the volume fractions of monomer i in phases j and k, respectively.

Neglecting the volume fraction of water in the monomer droplets, the following equation can be written when the first monomer droplet is formed:

$$\phi_A^D + \phi_B^D = 1 \qquad (11)$$

Under equilibrium conditions, eq. (10) allows one to express ϕ_i^D in terms of the concentration of monomer i in the polymer particles as follows:

$$\phi_i^D = \frac{k_{D,W}^i}{k_{P,W}^i} \nu_i [i]_p \qquad (12)$$

where ν_i is the molar volume of monomer i. Taking into account that the formation of monomer droplets was not allowed, combination of eqs. (11) and (12) led to the following constraint:

$$\frac{k_{D,W}^A}{k_{P,W}^A} \nu_A [A]_p + \frac{k_{D,W}^B}{k_{P,W}^B} \nu_B [B]_p \le 1 \qquad (13)$$

In addition, constrains (9) and (13) can be combined as follows:

$$[A]^P\left(\frac{k_{D,W}^A}{k_{P,W}^A} \nu_A + \frac{k_{D,W}^B}{k_{P,W}^B} \frac{\nu_B}{\beta(X_T)}\right) \le 1 \qquad (14)$$

(iii) *The monomer already charged into the reactor cannot be removed.*

The following two constraints can be written for monomers A and B:

$$\frac{\partial[\text{total monomer } A \text{ in the reactor}]}{\partial[\text{conversion}]} \ge 0 \qquad (15)$$

$$\frac{\partial[\text{total monomer } B \text{ in the reactor}]}{\partial[\text{conversion}]} \ge 0 \qquad (16)$$

The monomer added into the reactor may be as a free monomer or converted to copolymer. Consequently, eqs. (15) and (16) can be written as follows:

$$\frac{\partial A_f}{\partial X_T} + \frac{\partial A_{\text{pol}}}{\partial X_T} \ge 0 \qquad (17)$$

$$\frac{\partial B_f}{\partial X_T} + \frac{\partial B_{\text{pol}}}{\partial X_T} \ge 0 \qquad (18)$$

where A_f and B_f are the amounts of monomers A and B per cm^3 of water present in the reactor as a free monomers, and i_{pol}, the amount of monomer i incorporated to the copolymer. At any conversion, A_{pol} and B_{pol} are calculated as follows:

$$A_{\text{pol}} = \bar{Y}_A(X_T)X_T(A_T + B_T) \qquad (19)$$

$$B_{\text{pol}} = [1 - \bar{Y}_A(X_T)]X_T(A_T + B_T) \qquad (20)$$

where $\bar{Y}_A(X_T)$ is the cumulative composition in the copolymer at a conversion X_T given by

$$\bar{Y}_A(X_T) = \frac{1}{X_T} \int_0^{X_T} Y_A(X_T)\, dX_T \tag{21}$$

If monomer droplets are not present in the reactor, the free monomer (A_f and B_f) has to be in the latex particles or in the aqueous phase:

$$i_f = [i]_p V_p + [i]_w V_w \tag{22}$$

where V_p and V_w are the volumes of the monomer swollen polymer particles and aqueous phase per cm^3 of water, respectively, given by

$$V_p = \frac{V_{\text{pol}}}{1 - [A]_p \nu_A - [B]_p \nu_B} \tag{23}$$

$$V_w = \frac{W}{1 - \dfrac{[A]_p \nu_A}{k_{PW}^A} - \dfrac{[B]_p \nu_B}{k_{PW}^B}} \tag{24}$$

where W is the volume of water (1 cm^3), and V_{pol}, the volume of the polymer per cm^3 of water:

$$V_{\text{pol}} = V_{\text{seed}} + \frac{A_{\text{pol}} M_{W_A} + B_{\text{pol}} M_{W_B}}{\rho_P} \tag{25}$$

where ρ_P is the density of the copolymer.

(iv) *The maximum amount of monomer* i *that can be in the reactor at any conversion is the total amount of this monomer in the recipe,* i_T:

$$i_f + i_{\text{pol}} - i_T \leq 0 \tag{26}$$

To carry out the optimization, eq. (4) was approximated by means of the Simpson rule using n subintervals:

$$F \approx \frac{1}{3n} \left[\frac{1}{R_{p0}} + 4 \frac{1}{R_{p1}} + 2 \frac{1}{R_{p2}} \right.$$
$$\left. + \cdots + 2 \frac{1}{R_{pn-2}} + 4 \frac{1}{R_{pn-1}} + \frac{1}{R_{pn}} \right] \tag{27}$$

and a standard nonlinear programming (NLP) solver was used to minimize the objective function F subjected to the restrictions (9), (14), (17), (18), and (26) in all of the quadrature points. The concentration of the monomer A in the polymer particles, $[A]_p$, was chosen as the optimization variable. The opti-

mization problem can be formulated to obtain the discrete values of $[A]_p$ at the quadrature points. However, in this work, $[A]_p$ was expressed as a polynomial and the polynomial coefficients determined. To carry out the optimization, the overall polymerization rate has to be calculated. Therefore, $\bar{n}(X_T)$, which, in turn, depends on the time evolution of the initiator concentration, is required. This was solved by using the algorithm presented in Figure 1.

To apply the algorithm, a mathematical model for the system is required. In the examples given below, the mathematical model summarized in the Appendix with the values of the parameters given in Table I was used. The optimization algorithm presented in Figure 1 provides the time-evolution concentrations of both monomers in polymer particles and the aqueous phase as well as that of the monomer amounts incorporated into the copolymer. This allows one to calculate the total amount of each monomer in the reactor at any time. Differentiation of these values gives the feed rate profile of each monomer. The evolution of the overall conversion is asymptotic to 1; therefore, the end of the process
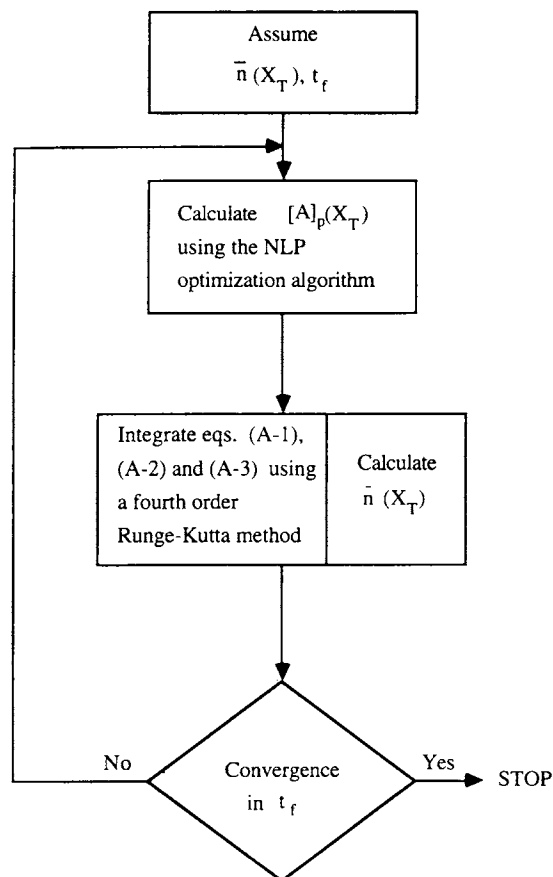

Figure 1 Optimization algorithm.

Table I Values of the Parameters Used in the Mathematical Model

$k_{p_{AA}}, k_{p_{AB}}, k_{p_{BA}}, k_{p_{BB}}$ (Refs. 9 and 10) (cm³ mol⁻¹ s⁻¹)	2.47×10^5	12.35×10^5	6.433×10^5	4.825×10^5
$k_{t_{AA}}, k_{t_{AB}}, k_{t_{BB}}$ (Refs. 10 and 11) (cm³ mol⁻¹ s⁻¹)	5.0×10^6	1.0×10^9	2.0×10^{11}	
$k_{f_{AA}}, k_{f_{AB}}, k_{f_{BA}}, k_{f_{BB}}$ (Ref. 12) (cm³ mol⁻¹ s⁻¹)	34	31.29	31.29	28.8
k_I (s⁻¹) (Ref. 4)	2.33×10^{-5}			
$k_{D,W}, k_{D,W}, k_{P,W}, k_{P,W}$ (Ref. 13)	714	2618	464	1570
D_{pi}, D_{wi} (cm² s⁻¹) (Refs. 9–15)	1.0×10^{-7}	1.0×10^{-5}		
v_a, v_b (cm³ mol⁻¹)	142.2	114.8		
M_{W_A}, M_{W_B} (g mol⁻¹)	128.17	104		
ρ_{P_A}, ρ_{P_B} (g cm⁻³) (Ref. 16)	1.026	1.065		
r_A, r_B (Ref. 17)	0.2	0.75		
f, Fabs	0.4	$6. \times 10^{-3}$		
N_p (part. cm⁻³ of water)	1.41×10^{17}			
dp (nm), Sc (g cm⁻³ of water)	68	0.33		

was considered to be when the overall conversion was 0.98.

POWER FEED METHOD

The results obtained with the optimal monomer addition policy were compared with those obtained with the power feed method. In the power feed method, the total monomer feed rate was chosen to be constant and the composition of the feed rate equal to the desired instantaneous composition of the copolymer. The monomer feed rates were calculated as follows:

$$F_T = F_A + F_B = \frac{A_T + B_T}{t_f} \qquad (28)$$

$$\frac{F_A}{F_B} = \frac{Y_A}{(1 - Y_A)} \qquad (29)$$

$$Y_A = Y_A\left(\frac{t}{t_f}\right) \qquad (30)$$

where t_f is the feed time. The total process time included the feed time and the time that the polymerization proceeded in the batch after the feed period. This batch time is needed to achieve a high conversion.

CASE STUDIES

Let us consider the emulsion copolymerization of butyl acrylate (A) and styrene (B) and assume that the instantaneous copolymer composition profiles

referred to butyl acrylate which are presented in Figure 2 are desired. These profiles include a profile that goes through a maximum (profile 1) as well as continuously increasing (profile 2) and decreasing (profile 3) copolymer composition profiles. Figure 3 presents the concentrations of monomers A (butyl acrylate) and B (styrene) in the polymer particles and its ratio calculated by the optimization algorithm for profile 1 using the mathematical model detailed in the Appendix and the parameters given in Table I. It can be seen that the $[A]_p/[B]_p$ profile showed a maximum similar to that of the desired composition. Figure 4 presents the time evolution of the amounts A_f and B_f as free monomers and the amounts of these monomers incorporated in the copolymer (A_{pol}, B_{pol}). The addition of these values
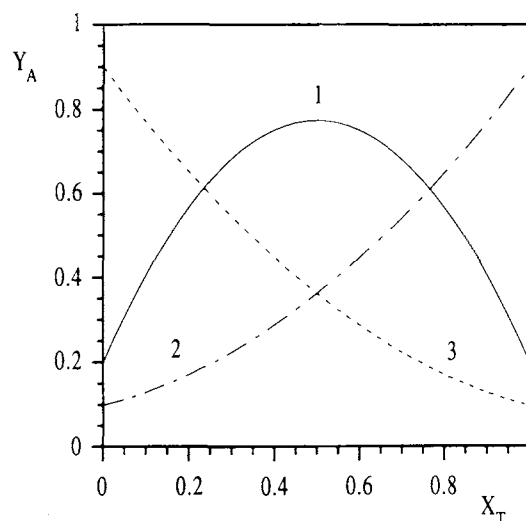

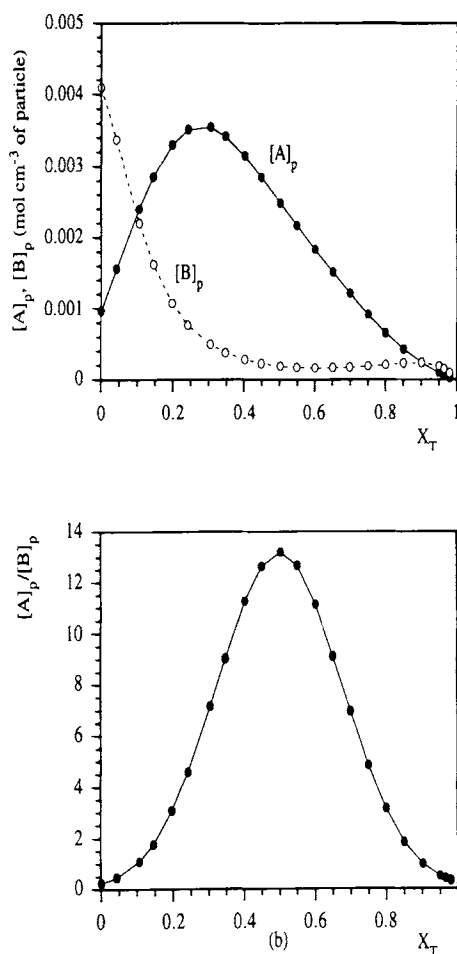**Figure 2** Desired copolymer composition profiles.

Figure 3 Concentrations of the monomers in the polymer particles calculated by the optimization algorithm for profile 1: (a) profiles of $[A]_p$ and $[B]_p$; (b) $[A]_p/[B]_p$ profile.

Figure 4 Time evolution of the amounts of monomers A and B for profile 1.

gave the total amounts of butyl acrylate and styrene that should have been fed into the reactor at a given time (A_R, B_R) to obtain a copolymer with composition profile 1 in Figure 2. Differentiation of these profiles gave the monomer feed rates presented in Figure 5. It can be seen that all the monomer A had to be fed into the reactor during the first fifth part of the process. The moment in which all the monomer A was in the reactor corresponded closely to that in which the maximum of the copolymer composition profile was reached.

Figure 6 presents the evolution of the concentrations of the monomers in the polymer particles and its ratio calculated by the optimization algorithm for profile 2. It can be seen that the $(A)_p/(B)_p$ evolution is similar to profile 2. Figure 7 presents the feed rate profiles for the optimal process to obtain copolymer composition profile 2. Figures 8 and 9 show the results corresponding to profile 3. It has
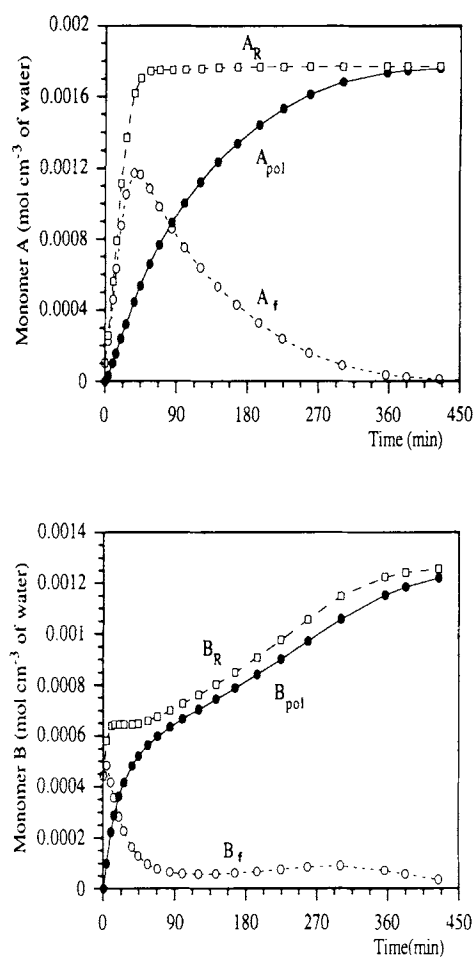

Figure 5 Feed rate profiles that give copolymer composition profile 1 in a minimum process time.
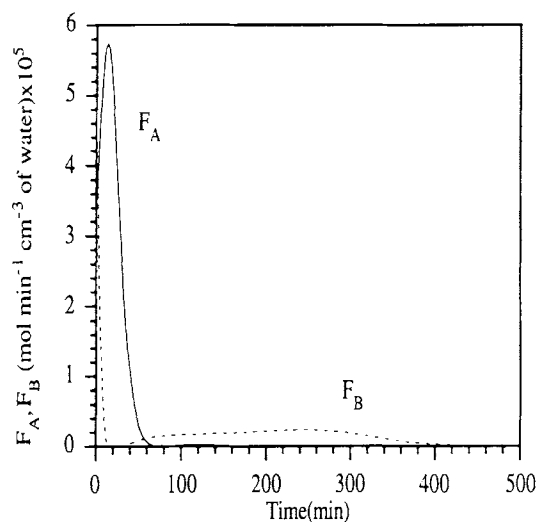
Figure 7   Feed rate profiles that give copolymer composition profile 2 in a minimum process time.
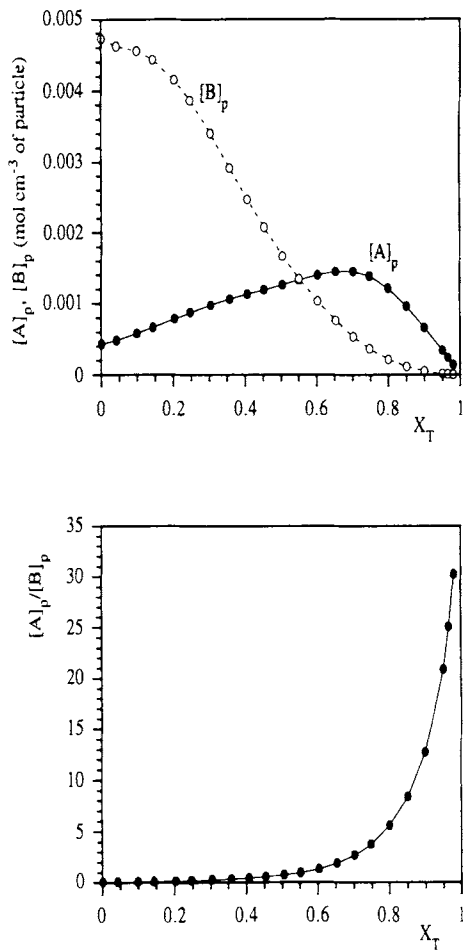

Figure 6   Monomer concentration in the polymer particles calculated by the optimization algorithm for profile 2: (a) profiles of $[A]_p$ and $[B]_p$; (b) $[A]_p/[B]_p$ profile.

to be pointed out that in this case the desired copolymer composition profile could be obtained by including all the less reactive monomer in the initial charge with some amount of the more reactive monomer and feeding the rest of the more reactive monomer at an adequate rate. However, by carrying out the polymerization in this way, monomer droplets will be present in the reactor at the beginning of the process.

It is interesting to compare the simulated instantaneous copolymer composition profiles obtained by this approach with those obtained using the power feed method. Figure 10 presents this comparison for profile 1. It can be seen that while the desired copolymer composition profile was obtained using the present approach significant deviations were found for the power feed method using a total process time (t_{pf}) equal to that of the optimal process. The deviations were less pronounced but still noticeable
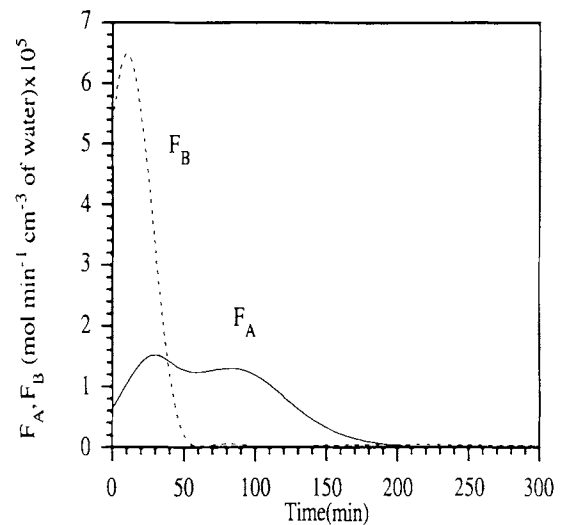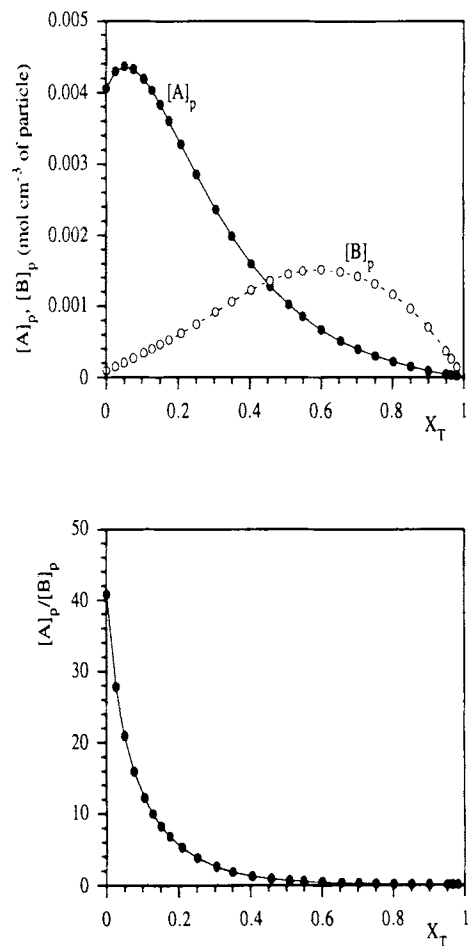

Figure 8   Monomer concentration in the polymer particles calculated by the optimization algorithm for profile 3: (a) profiles of $[A]_p$ and $[B]_p$; (b) $[A]_p/[B]_p$ profile.
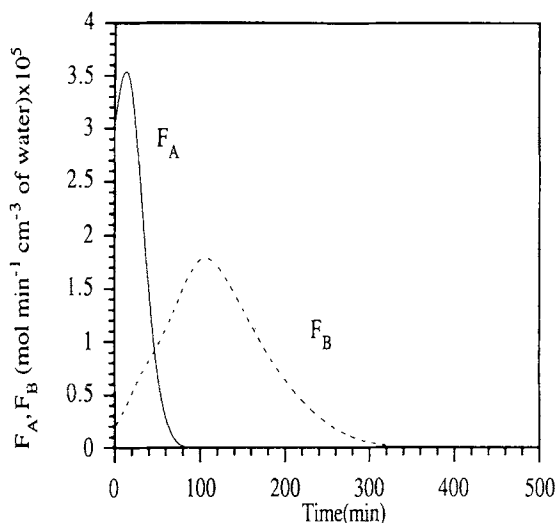
Figure 9 Feed rate profiles that give copolymer composition profile 3 in a minimum process time.

when a process time double that of the optimal one was used in the power feed method. Figures 11 and 12 show that for profiles 2 and 3 the optimal process provided always a better copolymer composition profile but the differences with the power feed method were less pronounced than for profile 1.

It has to be pointed out that in the calculations carried out in this article it was assumed that both the kinetic model and the values of its parameters were available. However, this is not usually the case for a real emulsion copolymerization system. The implementation of the present approach to real systems is presented in the second article of this series.

CONCLUSIONS

In the foregoing, a method for calculating the optimal monomer addition policy to produce emulsion copolymers with a given copolymer profile has been presented. The method allows the calculation of the time evolution of the monomer feed rates that ensures the formation of the desired copolymer composition profile in a minimum process time. The approach was applied by simulation to obtain widely different copolymer composition profiles in the emulsion copolymerization of butyl acrylate and styrene. In all cases, the desired instantaneous copolymer composition was obtained. The results obtained with the present approach were compared with those obtained using the power feed method. It was found that, using the same process time, the optimal process provided always a better copolymer composition profile than

did the power feed method. The composition drift depended on the desired copolymer composition profiles. In addition, the deviations were less pronounced but still noticeable when the total process time for the power feed method was twice that of the optimal process. To apply this method to a real system, the kinetic model and the values of the kinetic parameters have to be available. However, this is not usually the case for a real system. The implementation of the present approach to real systems is presented in the second article of this series.
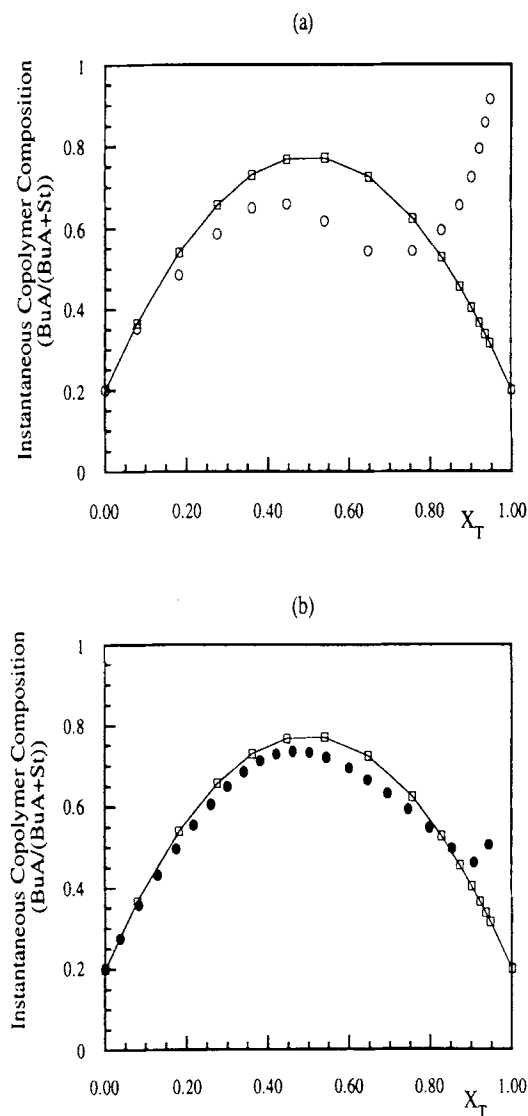

Figure 10 Comparison between the instantaneous co-polymer composition obtained by means of the optimal process and the power feed method for profile 1: (——) desired copolymer composition; ($\square$) optimal process; ($\bigcirc$) power feed method with $t_{pf} \simeq t_{opt}$; ($\bullet$) power feed method with $t_{pf} \simeq 2xt_{opt}$.
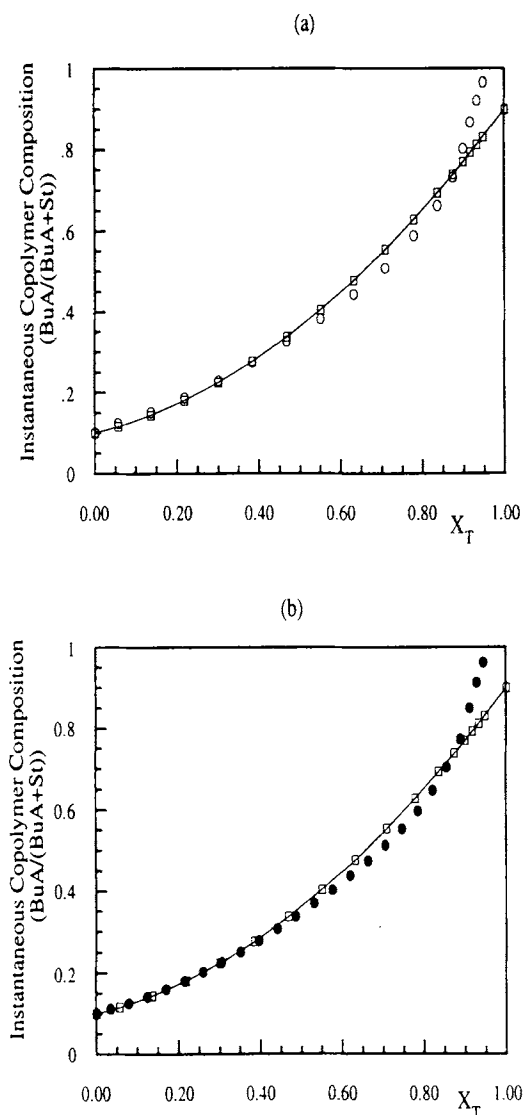
(a)

(b)

Figure 11   Comparison between the instantaneous co-
polymer composition obtained by means of the optimal
process and the power feed method for profile 2: (———)
desired copolymer composition; ($\square$) optimal process; ($\bigcirc$)
power feed method with $t_{pf} \simeq t_{opt}$; ($\bullet$) power feed method
with $t_{pf} \simeq 2xt_{opt}$.

NOMENCLATURE

a	parameter defined by eq. (A.5)
A_f, B_f	amounts of monomers A and B present in the reactor as free monomers (mol/cm^3 of water)
A_{pol}, B_{pol}	amounts of monomers A and B, respectively, incorporated into the copolymer (mol/cm^3 of water)

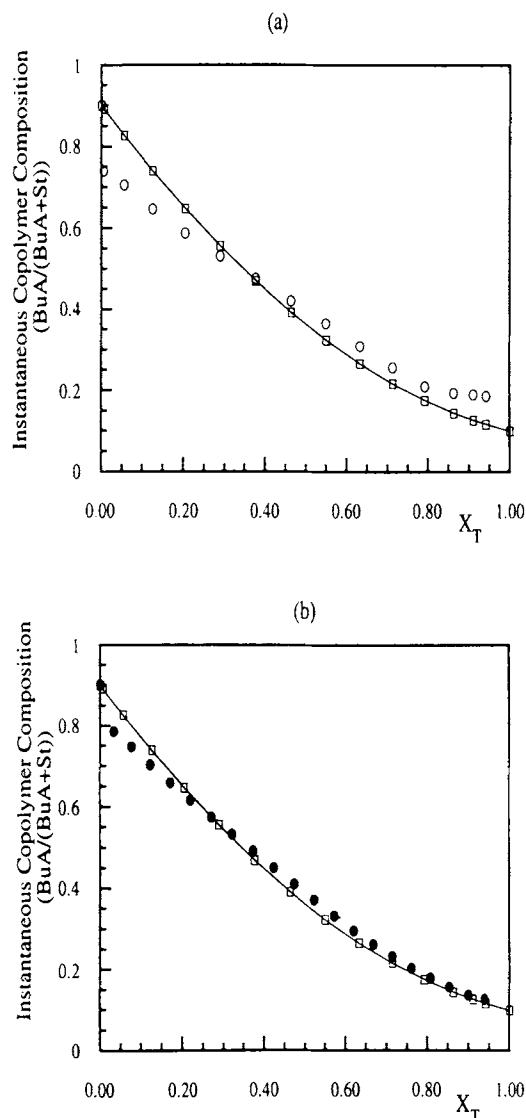|	
A_R, B_R	total amounts of monomers A and B present in the reactor (free monomer + polymer) at any time (mol/cm^3 of water)
A_T, B_T	total amounts of monomers A and B, respectively (mol/cm^3 of water)
c	parameter defined by eq. (A.7)
d_p	diameter of the monomer swollen polymer particles (cm)
D_W	average diffusion coefficient of oligomers in the aqueous phase (cm^2/s)

(a)

(b)

Figure 12   Comparison between the instantaneous co-
polymer composition obtained by means of the optimal
process and the power feed method for profile 3: (———)
desired copolymer composition; ($\square$) optimal process; ($\bigcirc$)
power feed method with $t_{pf} \simeq t_{opt}$; ($\bullet$) power feed method
with $t_{pf} \simeq 2xt_{opt}$.

D_{P_i}, D_{W_i} diffusion coefficients of a monomeric free-radical of type i in the polymer particles and in the aqueous phase, respectively (cm^2/s)

f efficiency factor for initiator decomposition

F objective function [eq. (4)]

F_{abs} efficiency factor for radical entry

$[i]_p$ concentration of monomer i in the polymer particles (mol/cm^3)

I_2 amount of initiator $(mol/cm^3$ of water)

k_a entry rate coefficient $(cm^3/mol\ s)$

k_d overall desorption rate coefficient $[s^{-1};$ eq. (A.9)]

k_{di} desorption rate coefficient of radicals of type i $[s^{-1};$ eq. (A.10)]

$k_{f_{ij}}$ chain transfer rate coefficient $(cm^3/mol\ s)$

k_I initiator decomposition rate constant (s^{-1})

$k_{j,k}^i$ partition coefficient of monomer i between phases j and k

$k_{p_{ij}}$ propagation rate constant $(cm^3/mol\ s)$

$\bar{k}_t$ average termination rate constant in the polymer particles $[cm^3/mol\ s;$ eq. (A.8)]

$\bar{k}_{tw}$ average termination rate constant in the aqueous phase $[cm^3/mol\ s;$ eq. (A.14)]

K_{0i} rate of exit of monomeric radicals of type i $[s^{-1};$ eq. (A.12)]

m parameter defined by eq. (A.6)

m_{di} partition coefficient of a monomeric radical of type i between polymer particles and aqueous phase

M_{Wi} molecular weight of monomer i (g/mol)

n no. subintervals in the Simpson rule [eq. (27)]

$\bar{n}$ average no. radicals per particle

N_P no. polymer particles per cm^3 of water

N_A Avogadro's number

P_i^j time-average probability of finding a growing chain with ultimate unit of type i in the phase j

r_A, r_B reactivity ratios

R_p overall polymerization rate $(mol/s\ cm^3$ of water)

R_{pi} polymerization rate of monomer i $(mol/s\ cm^3$ of water)

$[R]_w$ concentration of free radicals in the aqueous phase $(mol/cm^3$ of aqueous phase)

S_c solids content $(g/cm^3$ of water)

V_P volume of the monomer swollen polymer particles $(cm^3/cm^3$ of water)

V_{pol} volume of polymer $(cm^3/cm^3$ of water)

V_w volume of the aqueous phase $(cm^3/cm^3$ of water)

W volume of water $(1\ cm^3)$

X_T overall conversion

Y_A instantaneous copolymer composition

$\bar{Y}_A$ cumulative copolymer composition

$\bar{Y}_{A_T}$ average copolymer composition at the end of the process [eq. (1)]

Greek Symbols

β_i probability that a monomeric radical of type i reacts in the aqueous phase by either propagation or termination [eq. (A.11)]

$\beta(X_T)$ ratio $[A]_p/[B]_p$ that ensures the production of the desired copolymer composition profile [eq. (9)]

ϕ_r^j volume fraction of monomer i in phase j

ρ_p density of the polymer (g/cm^3)

ν_i molar volume of monomer i (cm^3/mol)

ν_p volume of one monomer swollen polymer particle (cm^3)

APPENDIX

The following mathematical model was used in the simulations:

Material Balances

$$\frac{dA_{pol}}{dt} = (k_{P_{AA}}P_A^P + k_{P_{BA}}P_B^P)[A]_P \frac{\bar{n}N_P}{N_A} \quad (A.1)$$

$$\frac{dB_{pol}}{dt} = (k_{P_{AB}}P_A^P + k_{P_{BB}}P_B^P)[B]_P \frac{\bar{n}N_P}{N_A} \quad (A.2)$$

$$\frac{dI_2}{dt} = -k_I I_2 \quad (A.3)$$

where I_2 is the amount of initiator per cm^3 of water, and k_I, the initiator decomposition rate constant, and the average number of radicals per particle, $\bar{n}$, was calculated by the approach proposed by Ugelstad and Hansen[18]:

$$\bar{n} = a^2/8/\{m + a^2/4/$$
$$[m + 1 + a^2/4/(m + 2 + \cdots)]\} \quad (A.4)$$

where

$$a^2 = 8k_a[R]_w/c \qquad (A.5)$$

$$m = k_d/c \qquad (A.6)$$

$$c = \bar{k}_t/v_P N_A \qquad (A.7)$$

where k_a is the entry-rate coefficient; $[R]_w$, the concentration of free radicals in the aqueous phase; k_d, the overall desorption rate coefficient; v_P, the volume of one monomer swollen polymer particle; N_A, the Avogadro's number; and k_t, the average termination rate constant given by

$$\bar{k}_t = k_{t_{AA}}(P_A^P)^2 + 2k_{t_{AB}}P_A^P P_B^P + k_{t_{BB}}(P_B^P)^2 \qquad (A.8)$$

The overall desorption rate coefficient is given by

$$k_d = k_{d_A} + k_{d_B} \qquad (A.9)$$

The rate coefficient for desorption of radicals of type i can be calculated as follows[19-21]:

$$k_{di} = (k_{fAi}P_A^p$$

$$+ k_{fBi}P_B^p)[i]_p$$

$$\times \frac{K_{0i}}{K_{0i}\beta_i + k_{piA}[A]_p + k_{piB}[B]_p} \qquad (A.10)$$

where k_{fij} are the chain-transfer rate coefficients; K_{0i}, the rate of exit of monomeric radicals of type i; and β_i, the probability that a monomeric radical of type i reacts in the aqueous phase by either propagation or termination given by

$$\beta_i = \frac{\begin{array}{l}k_{piA}[A]_w + k_{piB}[B]_w \\ + (k_{tiA}P_A^w + k_{tiB}P_B^w)[R]_w \phi_w^{aq}/V_w\end{array}}{\begin{array}{l}k_{piA}[A]_w + k_{piB}[B]_w \\ + (k_{tiA}P_A^w + k_{tiB}P_B^w)\dfrac{[R]_w \phi_w^{aq}}{V_w} + k_a \dfrac{N_p \phi_w^{aq}}{V_w N_A}\end{array}} \qquad (A.11)$$

Assuming a diffusion mechanism and no additional resistance in the interface, K_{0i} is given by the following equation[14]:

$$K_{0i} = \frac{12\dfrac{D_{wi}}{m_{di}d_p^2}}{1 + 2\dfrac{D_{wi}}{m_{di}D_{pi}}} \qquad (A.12)$$

where D_{wi} and D_{pi} are the diffusion coefficients of a monomeric radical of type i in the aqueous phase and the polymer particle, respectively; d_p, the diameter of the monomer swollen polymer particle; and m_{di}, the partition coefficient of such a radical between the polymer particles and the aqueous phase approximately given by k_{PW}^i. Assuming that radical entry occurs through diffusion, the entry rate constant is given by

$$k_a = 2\pi D_W d_p F_{abs} N_A$$

where D_W is the average diffusion coefficient of oligomers in the aqueous phase, and F_{abs}, the efficiency factor for radical entry.

Radical Balance in the Aqueous Phase

$$2f k_I I_2 + k_d \bar{n}\frac{N_P}{N_A} = k_a[R]_w \frac{N_P}{N_A} + 2\bar{k}_{tw}[R]_w^2 \qquad (A.13)$$

where f is the efficiency factor for initiator decomposition, and $\bar{k}_{tw}$, the average termination rate constant in the aqueous phase given by

$$\bar{k}_{tw} = k_{tAA}(P_A^w)^2 + 2k_{tAB}P_A^w P_B^w$$
$$+ k_{tBB}(P_B^w)^2 \qquad (A.14)$$

P_i^w is the probability of finding a free radical with ultimate unit for type i in the aqueous phase.

REFERENCES

1. J. Snuparek and F. Krska, *J. Appl. Polym. Sci.*, **21**, 2253 (1977).
2. J. Snuparek and F. Kaspar, *J. Appl. Polym. Sci.*, **26**, 4081 (1981).
3. D. R. Basset and K. L. Hoy, in *Process Description and Polymer Properties in Emulsion Polymers and Emulsion Polymerization*, D. R. Basset and A. E. Hamielec, Eds., ACS Symposium Series 165, American Chemical Society, Washington, DC, 1981.
4. M. S. El-Aasser, T. Makgawinata, J. W. Vanderhoff, and C. Pichot, *J. Polym. Sci. Polym. Chem. Ed.*, **21**, 2363 (1983).

5. S. C. Misra, C. Pichot, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci. Polym. Chem. Ed.,* **21,** 2383 (1983).

6. T. O. Broadhead, A. E. Hamielec, and J. F. MacGregor, *Makromol. Chem. Suppl.,* **10/11,** 105 (1985).

7. G. Arzamendi and J. M. Asua, *J. Appl. Polym. Sci.,* **38,** 2019 (1989).

8. J. Forcada and J. M. Asua, *J. Polym. Sci. Polym. Chem. Ed.,* **23,** 1955 (1985).

9. C. Walling, in *Free Radical in Solution,* Wiley-Interscience, New York, 1957.

10. M. Buback, L. H. García Rubio, R. G. Gilbert, D. H. Napper, J. Guillot, A. E. Hamielec, D. Hill, K. F. O'Driscoll, F. J. Olag, J. Shen, D. Solomon, G. Moad, M. Stickler, M. Tirrell, and M. A. Winnick, *J. Polym. Sci. Polym. Lett., Ed.,* **26,** 293 (1988).

11. I. Capeck, J. Barton, and E. Orolinova, *Chem. Zvesti,* **38,** 803 (1984).

12. J. Brandrup and E. H. Immergut, in *Polymer Handbook,* 2nd ed., Wiley-Interscience, New York, 1989.

13. J. L. Gardon, *J. Polym. Sci. Part A-1,* **6,** 2859 (1968).

14. M. Nomura, in *Emulsion Polymerization,* I. Piirma, Ed. Academic Press, New York, 1982.

15. F. K. Hansen and J. Ugelstad, in *Emulsion Polymerization,* I. Piirma, Ed. Academic Press, New York, 1982.

16. I. A. Maxwell, D. H. Napper, and R. G. Gilbert, *J. Chem. Soc. Faraday Trans. I,* **83,** 1449 (1987).

17. M. E. Cruz, J. Palacios, A. García Rejón, L. M. Ruiz, and L. Ríos, *Makromol. Chem. Suppl.,* **10/11,** 87 (1985).

18. J. Ugelstad and F. K. Hansen, *Rubb. Chem. J. Technol.,* **49**(3), 536 (1976).

19. J. M. Asua, E. D. Sudol, and M. S. El-Aasser, *J. Polym. Sci. Polym. Chem. Ed.,* **27,** 3903 (1989).

20. J. Forcada and J. M. Asua, *J. Polym. Sci. Polym. Chem. Ed.,* **28,** 987 (1990).

21. V. S. Rodríguez, J. M. Asua, M. S. El-Aasser, and C. A. Silebi, *J. Polym. Sci. Polym. Phys. Ed.,* **29,** 483 (1991).